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14. ABSTRACT

This project has developed a statistical learning approach to identify potential new high temperature ferroelectric piezoelectric perovskite compounds. Our predictions of the Curie temperature (Tc) ranging from 700C-1100C are the highest reported in either experimental or theoretical studies and the number of new proposed compounds based on our work nearly doubles the known candidate piezoelectric ferroelectric perovskites. Unlike most computational studies on crystal chemistry, where the starting point is some form of electronic structure calculation, we use a data driven approach to initiate our search. In parallel to the computational studies, we have developed a detailed experimental protocol for exploring the processing parameter space for synthesizing in a combinatorial fashion of known existing piezoelectric perovskites.. This provides strong evidence of the value of informatics to significantly accelerate materials discovery. Our experimental studies also provided us the framework to test our informatics based predictions. For instance we have synthesized BiLuO3-PbTiO3 and discovered that the system is indeed a perovskite structure as per our predictions and our measured Tc of ~ 550C though ~ lower than the ~ 700C of our predictions , is one of the highest reported

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Combinatorial and High Throughput Discovery of High Temperature Piezoelectric Ceramics

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Abstract

This project has developed a statistical learning approach to identify potential new high temperature ferroelectric piezoelectric perovskite compounds. Our predictions of the Curie temperature (T_c) ranging from 700C-1100C are the highest reported in either experimental or theoretical studies and the number of new proposed compounds based on our work nearly doubles the known candidate piezoelectric ferroelectric perovskites. Unlike most computational studies on crystal chemistry, where the starting point is some form of electronic structure calculation, we use a data driven approach to initiate our search. In parallel to the computational studies, we have developed a detailed experimental protocol for exploring the processing parameter space for synthesizing in a combinatorial fashion of known existing piezoelectric perovskites. We not only identified new compound chemistries with T_C exceeding known ferroelectric perovskite materials but also optimized the site occupancy of newly the identified new compound chemistries. This provides strong evidence of the value of informatics to significantly accelerate materials discovery. Our experimental studies also provided us the framework to test our informatics based predictions. For instance we have synthesized $BiLuO_3$-$PbTiO_3$ and discovered that the system is indeed a perovskite structure as per our predictions and our measured Tc of ~ 550C though lower than the ~ 700C of our predictions, is one of the highest reported experimental measurements reported in the literature. Given that our models are based solely on crystal and electronic structure data and did not microstructural or impurity chemistry information, this is a very promising result. To the best of our knowledge, this is the first direct attempt to experimentally validate informatics based structure-property predictions.

Executive Summary

This project has developed a statistical learning approach to identify potential new high temperature ferroelectric piezoelectric perovskite compounds. Unlike most computational studies on crystal chemistry, where the starting point is some form of electronic structure calculation, we use a data driven approach to initiate our search. This is accomplished by: identifying patterns of behavior between discrete scalar descriptors associated with crystal and electronic structure and the reported Curie temperature (T_c) of known compounds; extracting design rules that govern critical structure-property relationships; and discovering in a

quantitative fashion the exact role of these materials descriptors. Our approach applies linear and non-linear manifold methods for data dimensionality reduction to discover the dominant descriptors governing structure-property correlations and data mining methods to quantitatively assess the specific combination of descriptors that govern the link between crystal chemistry and T_c. We have used this information at the electronic and crystal structure level to develop predictive models that can suggest new structure/chemistries and/or properties. In this manner, our discoveries have included $BiTmO_3$-$PbTiO_3$ and $BiLuO_3$-$PbTiO_3$ which were predicted to have a T_c of 730 and 705 °C, and respectively. Expanding the chemical search space to nearly one million possible stoichiometries and using more complex statistical learning tools, we have also proposed over half a dozen binary cation ferroelectric perovskites with even higher Tc reaching as high as ~ 1100C. A quantitative structure-property relationship model similar to those used in biology and drug discovery, not only predicts our new chemistries but also validates published reports. Our predictions in terms of Tc are the highest reported in either experimental or theoretical studies and the number of new proposed compounds based on our work nearly doubles the known candidate ferroelectric perovskites. This provides strong evidence of the value of informatics to significantly accelerate materials discovery.

In parallel to the computational studies, we have developed a detailed experimental protocol for exploring the processing parameter space for synthesizing in a combinatorial fashion of known existing piezoelectric perovskites (e.g. $BiFeO_3$–$PbZrO_3$–$PbTiO_3$ ternary solid solution). The experimental work has laid out the details of tracking chemistries near the morphotropic

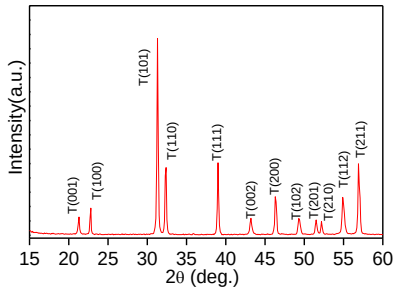
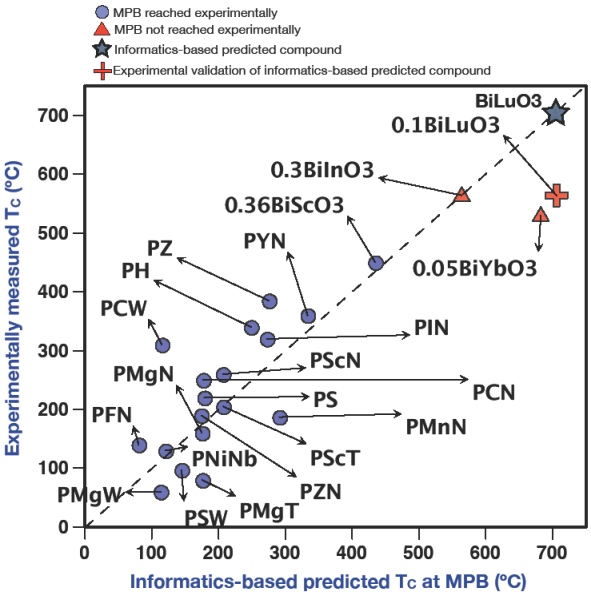


Fig. 1: Comparison of experimental results of Curie temperature of BiLuO3 with the informatics based prediction. While the Tc is lower than the prediction, this chemistry would not have been a target for exploration without the informatics prediction. However the perovskite structure prediction was confirmed experimentally. Another significant point is that this is the highest reported experimental values of Tc of ferroelectric perovskites



phase boundaries (MPB), and to empirically relate microstructural impact on phase stability and properties. The tradeoff between achieving the right crystal chemistry at the MPB with both a high permittivity with the constraints of being at the MPB and getting a high Tc

have been experimentally mapped. A higher rhombohedral/tetragonal phase ratio in the MPB region appears to be favorable for the ferroelectric and piezoelectric properties. Our experimental studies also provided us the framework to test our informatics based predictions. For instance we have synthesized $BiLuO_3$-$PbTiO_3$ and discovered that the system is indeed a perovskite structure as per our predictions and our measured Tc was ~ 550C. While this was lower than the ~ 700C of our predictions, this is one of the highest reported experimental measurements reported in the literature. Given that our models are based solely on crystal and electronic structure data and did not microstructural or impurity chemistry information, this is a very promising result. To the best of our knowledge, this is the first direct attempt to experimentally validate informatics based structure-property predictions.

With our initial discovery of new compounds at high temperatures we had restricted our search space of new $BiMEO_3$-$PbTiO_3$ to include: *ME*=Sc^{3+}, In^{3+}, Yb^{3+}, Lu^{3+} and Tm^{3+}. In the next phase of our work since our initial report we have included single *ME* cations with charge 3+ or a mixture of two cations with an average 3+ charge and that exhibit both strong and weak ferroelectric activity: Ga^{3+}, Mn^{3+}, Fe^{3+}, Al^{3+}, Hf^{4+}, Cr^{3+}, Co^{3+}, $(Zn_{1/2}Ti_{1/2})^{3+}$, $(Mg_{1/2}Ti_{1/2})^{3+}$, $(Mg_{3/4}W_{1/4})^{3+}$, $(Mg_{2/3}Nb_{1/3})^{3+}$, $(Zn_{3/4}W_{1/4})^{3+}$, $(Zn_{2/3}Nb_{1/3})^{3+}$, $(Zn_{1/2}Zr_{1/2})^{3+}$, $(Zn_{1/2}Sn_{1/2})^{3+}$, $(Sc_{1/2}Fe_{1/2})^{3+}$, $(Ni_{1/2}Ti_{1/2})^{3+}$, $(Sc_{3/4}Ga_{3/4})^{3+}$.

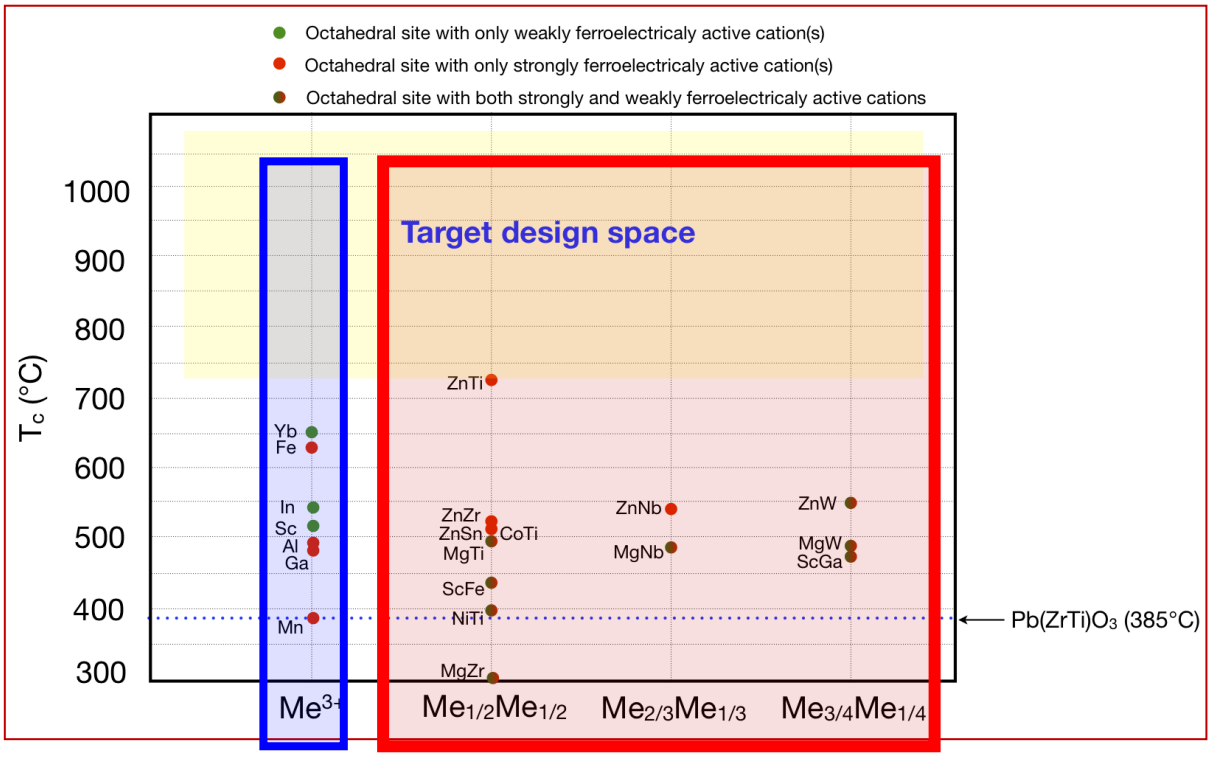


Fig. 2: The search space explored in the initial stages of the project is outlined in blue, and has been expanded into the region shaded in red. This has now increased the potential compound search space to over one million compounds.

Another new aspect of our modeling work is that enlarged the descriptor space to 48 descriptors and down selected them to 6 using PCA and Rough Sets data mining methods. The latter, i.e. Rough sets, is a new approach that accounts for uncertainty in our data sets. We employed non-linear artificial neural networks (ANN) method to develop the Quantitative Structure Property Relationships (QSPRs) for predicting the Curie temperature, T_C. 43 compounds were used for QSPR modeling. Given the vastly larger search space of compounds, we automated the process by employing Genetic Algorithm method. Our search space was greater than 10^6 potential compound chemistries. We not only identified new compound chemistries with T_C exceeding known ferroelectric perovskite materials but also optimized the site occupancy of newly the identified new compound chemistries

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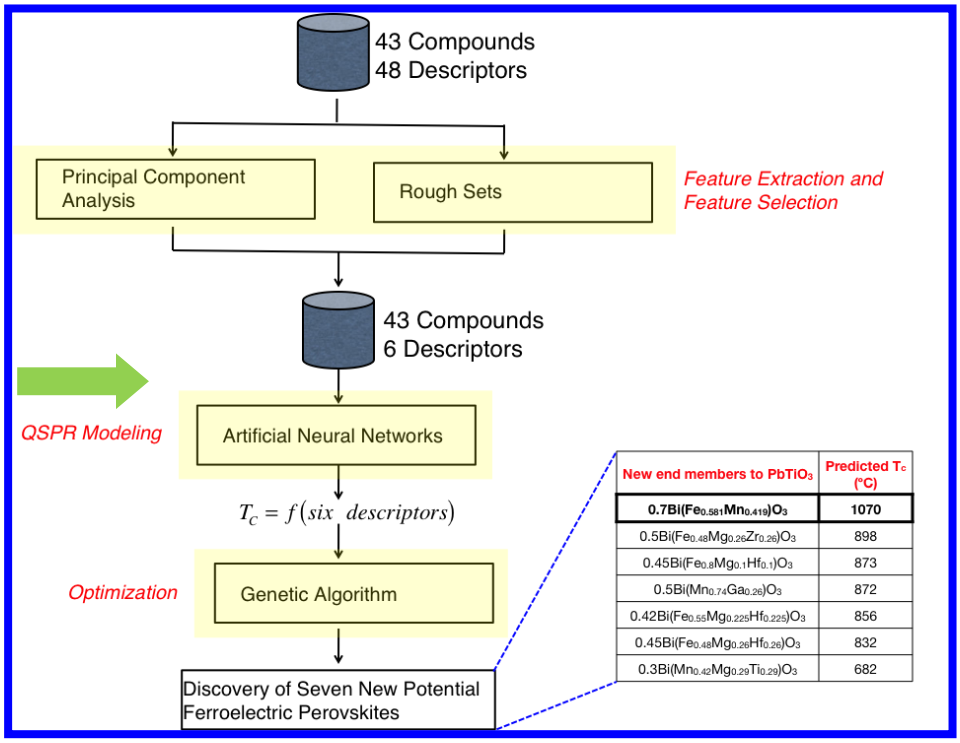
Fig. 3: During the optimization stage, we explored more than one million possible combinations of compound chemistries and identified seven *new compounds with high Tc. The seven potential ferroelectric perovskite chemistries are inscribed in the schematic shown above*



New end members to $PbTiO_3$	Predicted T_c (°C)
$0.7Bi(Fe_{0.581}Mn_{0.419})O_3$	**1070**
$0.5Bi(Fe_{0.48}Mg_{0.26}Zr_{0.26})O_3$	898
$0.45Bi(Fe_{0.8}Mg_{0.1}Hf_{0.1})O_3$	873
$0.5Bi(Mn_{0.74}Ga_{0.26})O_3$	872
$0.42Bi(Fe_{0.55}Mg_{0.225}Hf_{0.225})O_3$	856
$0.45Bi(Fe_{0.48}Mg_{0.26}Hf_{0.26})O_3$	832
$0.3Bi(Mn_{0.42}Mg_{0.29}Ti_{0.29})O_3$	682

Summary of Key Research Accomplishments

- Identified new candidate high temperature ferroelectric piezoelectrics
- Highest Tc predictions
- Defined quantitative structure-property correlations for materials discovery
- Established experimental protocol for exploring combinatorial bulk processing of ceramics
- Experimental validation of informatics based structure type prediction

- Informatics based trends for high temperature piezoelectric behavior observed experimentally

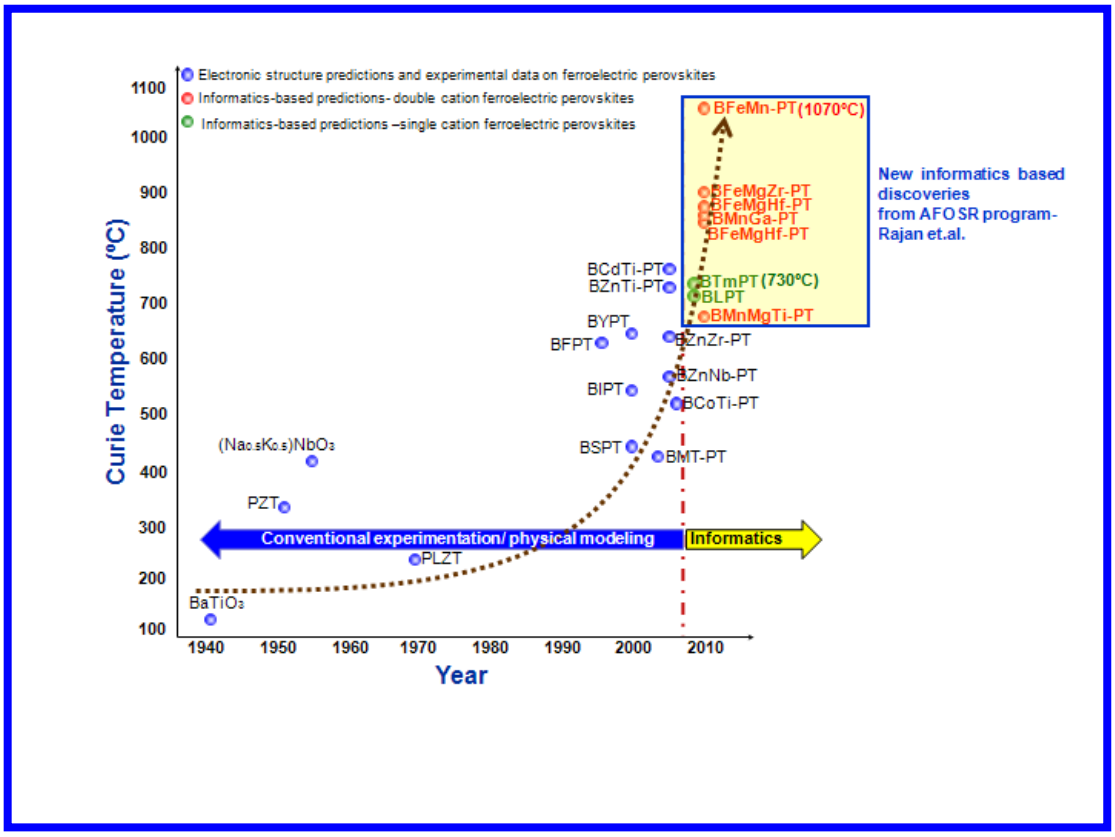


Fig. 4: Assessment of materials discovery for high temperature piezoelectric ferroelectric perovskites showing the striking impact of informatics, as developed in this program, on significantly accelerating and enlarging the materials design space for new high temperature multifunctional materials.

Personnel

2 PhDs have been based on this project:

- Wei Hu: "*Experimental Search for High Curie Temperature Piezoelectric Ceramics with Combinatorial Approaches*" -December 2011 graduation (Advisors: X. Tan and K. Rajan)
- Prasanna Balachandran: "*Statistical Learning for Chemical Crystallography*" -December 2011 graduation (Advisor: K. Rajan)

1 Post-doctoral scientist also assisted in this project- Dr. Scott Broderick (Advisor: K. Rajan)

Co-PIs: Krishna Rajan and Xiaoli Tan: Department of Materials Science and Engineering, Iowa State University, Ames IA.

Honors/ Awards

1. Wilkinson Professorship of Interdisciplinary Engineering -2011
2. CSIRO- Australia: Distinguished Visiting Scientist Fellowship Award- 2011
3. Akinc Research Award- Iowa State University-2009
4. Plenary Lecture Award: Society for Industrial and Applied Mathematics (SIAM) – Data Mining Conference: 2008

Publications (during course of research period)

1. **Learning from Systems Biology: An "omics" approach to materials design** Journal of Metals JOM 53-55 (March 2008)
2. **Materials Informatics parts I and II :** Guest editor: Krishna Rajan: *Journal of Metals, Materials & Minerals (JOM*) (March 2008 and January 2009)
3. **Materials Informatics***:* Guest editors: K. Rajan and P. Mendez: *Journal of Statistical Analysis and Data Mining : special issue* (April 2009 and June 2009)
4. **Principal Component Analysis and Dimensional Analysis as Materials Informatics Tools to Reduce Dimensionality in Materials Science and Engineering** Statistical Analysis and Data Mining J. ; Krishna Rajan, Changwon Suh and Patricio F. Mendez **1** 361-371 (2009)
5. **Data Mining and Inorganic Crystallography** in *Data Mining in Crystallography* ; Series: Structure and Bonding , Vol. 134 Hofmann, Detlef W.M.; Kuleshova, Liudmila N. (Eds.) pp.59-89; Springer-Verlag (2010)
6. **$BiFeO_3$–$PbZrO_3$–$PbTiO_3$ ternary system for high Curie temperature piezoceramics** Wei Hu, Xiaoli Tan and Krishna Rajan *Journal of the European Ceramic Society*, **31**, Pages 801-807 (May 2011)
7. **Identifying the "inorganic gene" for High Temperature Piezoelectric Perovskites through Statistical Learning** P. Balachandran, S.R. Broderick and K. Rajan; *Proceeding Royal Society A* **467:** 2271-2290 (August 8, 2011)
8. **Combinatorial Materials Libraries: Review of State of the Art***:* Radislav Potyrailo, Krishna Rajan, Klaus Stoewe, Ichiro Takeuchi, Bret Chisholm, and Hubert Lam; *ACS Combinatorial Sciences* (in press- **DOI:** 10.1021/co200007w)
9. **Classification of Oxide Compounds through Data-Mining Density of States Spectra** *J.* , Scott R. Broderick, Hafid Aourag and Krishna Rajan *; Amer. Ceramic Society* **94**, Issue 9, Pages: 2974–2980 (September 2011)
10. **Piezoelectric Ceramics with Compositions at the Morphotropic Phase Boundary in the $BiFeO_3$–$PbZrO_3$–$PbTiO_3$ Ternary System** Wei Hu, Xiaoli Tan and Krishna Rajan *J. Amer. Ceramic Society* Article first published online : 1 JUL 2011, DOI: 10.1111/j.1551-2916.2011.04715.x

11. **Ontology Engineering: Computational Informatics for Materials Discovery** –K. Rajan in *Models, Databases, and Simulation Tools Needed for the Realization of Integrated Computational Materials Engineering* pp. 73-81 eds. S. Arnold and T.Wong –ASM International- Materials Park ,OH (2011)
12. **Materials informatics as a computational infrastructure for materials discovery** P V Balachandran and K Rajan *in Proc. SciDAC 2011*, Denver, CO, July 10-14, 2011, http://press.mcs.anl.gov/scidac2011/
13. **A comparative study of experimental and informatics based prediction of high-temperature ferroelectric perovskites** Wei Hu, Prasanna V. Balachandran, Scott R. Broderick, Xiaoli Tan and Krishna Rajan – *J. European Ceramic Society*- submitted
14. **"Omics" based computational design of very high temperature piezoelectric perovskites** –P. Balachandran ,P. Das, S.Gangulay, S. Datta and K. Rajan *J. American Ceramic Society***-** in preparation

Invited/ Plenary Presentations (last 12 months)

1. **Informatics for Discovering the Inorganic Gene in Complex Inorganic Solids**
   Workshop on Evolution and Control of Complexity: key experiments using hard X-rays
   Advanced Photo Source, Argonne IL October 12, 2010- K. Rajan

2. **Ontology Engineering : computational informatics for an ICME infrastructure**
   MS&T meeting- Houston, TX, October 18, 2010- K. Rajan

3. **Informatics for Nanomaterials Discovery and Design**
   Nanoinformatics 2010
   Arlington, VA, Nov. 4, 2010- K. Rajan

4. **Informatics for Materials Chemistry and Chemical Imaging**
   Pacific Northwest National Laboratory
   Richland, WA, January 20th 2011- K. Rajan

5. **Crystal Chemistry and Imaging through Information Science**
   Colorado School of Mines, Golden CO. -February 4th, 2011- K. Rajan

6. **Accelerated Insertion of Materials with Incomplete or Uncertain Information**
   TMS Annual Meeting- San Diego CA- February 28th 2011- K. Rajan

7. **Materials Informatics: facilitating engagement for materials discovery**
   Materials Informatics workshop- CSIRO Center for Materials Science and Engineering
   Clayton, Victoria, Australia- May 17th 2011- K. Rajan

8. **Materials Informatics: harnessing data for materials discovery**
   CSIRO Advance Materials Conference- Plenary lecture
   Melbourne, Australia- May 23rd 2011- K. Rajan

9. **Statistical Learning for Materials Discovery**
   Materials Informatics Symposium- Tools for Design and Discovery
   Centre Européen de Calcul Atomique et Moléculaire (CECAM)
   Lausanne, Switzerland - May 24th 2011 - K. Rajan

10. **Multiscale Materials Modeling with the "Right Stuff": data mining to rank information**
    Los Alamos National Laboratory Workshop- Uncertainty Quantification and Multiscale Materials Modeling
    Santa Fe, NM. - June 13th 2011- K. Rajan

11. **Materials Informatics as a Computational Infrastructure for Materials Discovery**
    Scientific Discovery through Advanced Computing (SciDAC) 2011 Conference-Plenary lecture
    Denver, CO. July 12th 2011- K. Rajan